ARKIV FÖR FYSIK Band 18 nr 19

Communicated 24 February 1960 by E. Rudberg and K. Siegbahn

Investigations of the structure of the bremstrahlung-isochromats of W, Mo and Ta

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With 17 figures in the text

ABSTRACT

The structure near the short-wavelength limit of the continuous X-ray spectrum has been investigated, using a concave crystal spectrometer with a Geiger counter. The isochromats found (for W, Mo and Ta at ~ 3.7 kV) are interpreted by comparisons with characteristic energy loss spectra and X-ray absorption spectra. Angular and voltage dependence of the structure are discussed. A new method of determining $V\lambda_s$ (h/e) with great accuracy is demonstrated.

A new procedure for precision measurement of high voltages has been developed (accuracy 2:100000).

Introduction

The continuous X-ray spectrum in the neighbourhood of the short-wavelength limit has always been a subject of great interest. Most of the investigations made in this field have been carried out in order to make a determination of h/e. As Du Mond [1] has pointed out the quantity actually measured is the *voltage–wavelength conversion factor* $V\lambda_s$, where V is the voltage over the X-ray tube corresponding to the short-wavelength limit λ_s measured in the Siegbahn X-unit scale.

In studying the short-wavelength limit one usually uses a monochromator with as small a window curve as possible, selects a known wavelength, and applies a very stable DC high voltage to an X-ray tube. A spectrum (a so-called *isochromat*) can be formed by varying the voltage. The general appearance is seen in Fig. 1. If the wavelength and the high voltage are measured with very high precision, the problem to determine $V\lambda_s$ (or h/e) is then reduced to finding that point on the isochromat which corresponds to the actual wavelength.

Early investigators working with bad spectral and voltage resolution and using large voltage steps (10–50 volts) did not find any structure near the limit and simply used the extrapolated value for the calculation of h/e (or $V\lambda_s$). A large step forward was taken by Ohlin in 1941 when he used 2-volt steps with good spectral and voltage resolution. He then found the well-known structure in Fig. 1, and he also used the extrapolated value.

Later works [1, 3, 4] have shown that it is very difficult to find the exact threshold of the quantum limit without having a correct explanation of the structure near the limit. The method for the location of the limit used by du Mond [1, 3, 4, 6] and others in later works must nowadays be looked upon as very unsatisfactory. This method

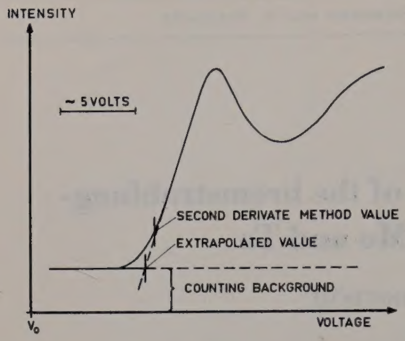

Fig. 1. A typical isochromat for tungsten.

consists in choosing a point on the isochromat where the second derivative is at a maximum.

As shown in this investigation and also by Ulmer and Vernickel [5], the structure is extraordinarily pronounced, a phenomenon which du Mond's method does not take into account.

Because of the great difficulty of treating the problem theoretically, more experimental work is needed in order to arrive at a complete explanation of the structure. Some interesting results have been found in this work.

The chief advantage of the apparatus used in the present experiment is the high intensity of the spectrometer. It is, in fact, about five times as intense as those used by Ulmer and Vernickel [5] or by Bearden [3, 4]. This has been achieved by using a *curved* crystal, choosing a suitable crystal and Geiger counter and by adjusting the spectrometer properly.

The resolving power is not extremely high (~ 2.5 volts at 4kV). However, Bearden and Schwartz found a width of about 4 volts for the first peak in their isochromats (at 6 kV) in spite of the fact that they used a monochromator width of ~ 0.5 V. Therefore the disadvantage arising from the comparatively low resolving power of the spectrometer used in the present work is not so serious.

Thanks to the high intensity, it was possible to record a whole curve in a few hours while still keeping the statistical error small. This is rather important because finer details in the isochromats may be lost if the number of points per voltage interval or the number of counts per point is reduced.

Experimental arrangements

The spectrometer

A spectrometer with curved crystal and Geiger counter was used. The principle and construction of a similar spectrometer has already been described in detail by Ohlin [2]. Therefore only those parts which are of special interest for this investigation will be described here.

The vacuum tank was made of aluminium and was provided with two large windows of perspex at both ends, thus making it possible to observe the focal spot and the scale of the micrometer screw from the outside. The spectrometer was made vacuum tight by means of rubber rings.

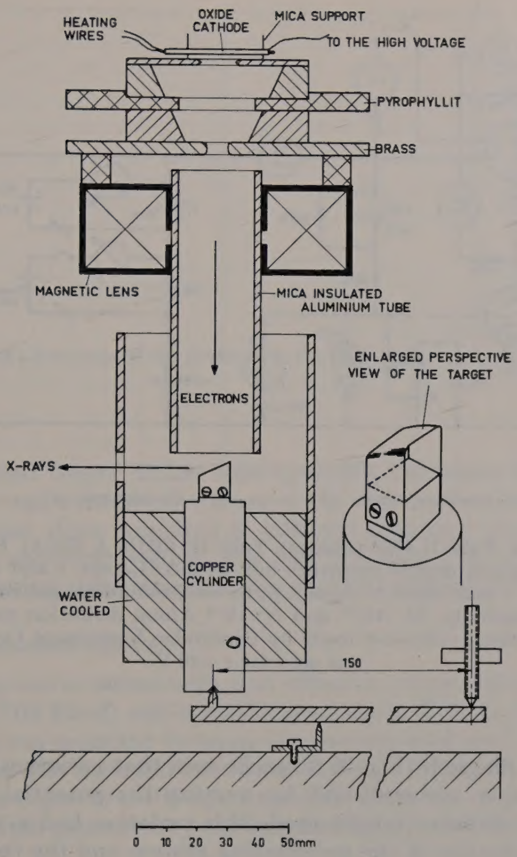

Fig. 2. The X-ray tube.

Through rotatable vacuum connections, the height position of the target, the angular position of the X-ray tube, and the micrometer screw (which determines the position of the detector slit) could be adjusted externally.

The X-ray tube

The X-ray tube is shown in Fig. 2. The oxide cathode was taken from an ordinary rectifier tube (5V4 G). The cathode consisted of a small nickel tube and was heated indirectly by means of an insulated tungsten wire fed by a high-tension insulated transformer. One end of the heating wire was connected to the high voltage outside the vacuum tank.

The electron beam was focused on the target by the accelerating system and further by a magnetic lens. At 10 mA emission, the current loss to the anode was only 0.2 mA. The focal spot was about 2.5 × 5 mm in size.

The aluminium tube was held at −150 V with respect to the anode to reduce the number of stray electrons.

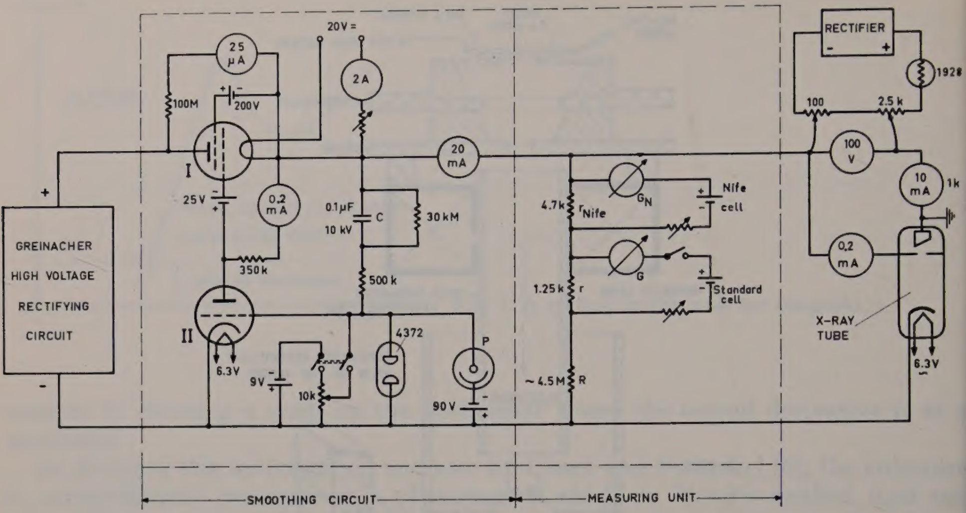

Fig. 3. Circuit diagram. Tube I: 4650 (Philips). Tube II: 6BD4 A (RCA). *P*, Cetron photocell 1 V AB. r_{Nife}, Wolff manganin decade resistance box with 0.01-steps. *r* and *R*, manganin precision resistors; see also Fig. 7 and Table 2. G_N and *G*, moving-coil mirror galvanometers; internal resistances 450 Ω and sensitivity 20×10^{-9} and 5×10^{-9} A/mm deflection respectively. The 100-V instrument was a precision voltmeter made by Cambridge Instrument Co. Ltd. The 50-V range was used for $v < 40$ V.

From the circuit diagram (Fig. 3) it can be seen that variation of the total voltage of the X-ray tube is accomplished by varying the potential of the target only. Owing to the large distance target–anode this variation had a very small influence on the focusing properties of the accelerating system and the emission current.

Though stabilised AC current was used for heating the cathode, the emission current was not extremely stable. However by regulating the primary voltage of the transformer by hand the emission current could be kept constant within 0.5 %. Operating the tube in the space charge region was avoided, since this might increase the effective work function of the cathode.

The anticathode consisted of a small plate (W 0.04 mm, Mo 0.20 mm, and Ta 0.06 mm) fastened by screws as shown in Fig. 2. The resistance of the plate at operating temperature could be ignored.

To avoid heat radiation from the target (at ~ 1200°) to the crystal a small aluminium window, 0.5 μ thick, was mounted between target and crystal.

The crystal and crystal holder

The crystals were bent in steel holders with precision ground cylindrical surfaces of 1000 mm radius. To control the temperature of the crystal one joint of a thermoelement was welded to a piece of copper, the latter being in thermal contact with the crystal holder. The other joint was placed in a constant temperature bath.

The opening of the crystal holder was 1.5×12 mm and the dimension of the crystal (quartz $10\bar{1}1 : d_1 = 3335.74$ XU) was $15 \times 25 \times 0.5$ mm.

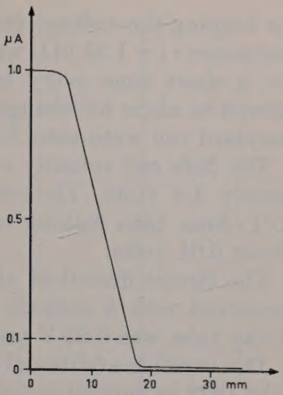

Fig. 4. Photo-current as a function of the position of the light spot.

The Geiger counter

A halogen-quenched Geiger Müller tube type MX 118 made by Mullard Limited was used. This tube had a threshold voltage of 980 volts and a plateau length of about 200 volts. The plateau slope measured at different occasions was found to be 5–7 % per 100 volts. The operating voltage was 1050 ± 5 volts. The dead-time measured was 260 μsec. The pulses were recorded by a Philips scaler type PW 4032.

The pumps and evacuation system

The high vacuum was obtained with a oil diffusion pump (Balzers DIFF 500 filled with Dow Corning 703 Fluid) and a mechanical pump (Balzers DUO 25).

A liquid air trap was mounted between the vacuum tank and the diffusion pump. The vacuum system also included two vacuum-meter tubes, one Pirani gauge, and one ionisation gauge (Speedivac JG-2H) mounted on the top of the vacuum tank.

The working vacuum measured by the ionisation gauge was about 3×10^{-6} mm Hg.

The high voltage equipment

The circuit diagram is shown in Fig. 3. The smoothing circuit has been described previously by Ohlin [2]. It consists of two tubes, tube I (4650) in series and tube II (6BD4 A) parallel with the high voltage. Tube II works as a resistance amplifier by means of which a change in output voltage is fed back to the grid of tube I. In this way any changes in input voltage are almost completely absorbed by tube I. Stabilisation will take place only if the voltage over the condenser C is constant.

To compensate for the leakage in the condenser a photocell P is incorporated in the circuit. The photocell is illuminated by the lightspot of the galvanometer G_N. The current delivered by the photocell as a function of the position of the lightspot (about 12 × 12 mm in size) is shown in Fig. 4. In this figure it can be seen that a leakage current of at least 0.1 μA is required for good stabilisation. Since the natural leakage of the condenser was only 0.01 μA, a leakage resistance of about 30 k$\mathrm{M}\Omega$ was connected across the condenser.

One way to measure the high voltage is to use the Nife cell as a secondary standard and to measure the ratio R/r_{Nife}. However, this method introduces an error in the measurement of the e.m.f. of the Nife cell. Moreover, this type of cell is not as stable as a standard cell. Therefore the Nife cell was not used for measurement but only for keeping the voltage at a constant value. For measurement a standard cell and a resistance r ($= 1.25$ kΩ) was included in the circuit. This standard cell was connected for a short time every ten minutes and when necessary the resistance r_{Nife} was altered to allow for changes in the e.m.f. of the Nife cell. The Nife cell as well as the standard cell were sunk into Dewar bottles filled with transformer oil.

The Nife cell actually consisted of three cells in series with an e.m.f. of approximately 3.8 volts. The resistance r_{Nife} of about 4.70 kΩ could be varied in steps of 0.01 ohms, thus making it possible to vary the high voltage (~ 3700 V) in steps of about 0.01 volts.

The circuit described above was extremely stable, 1:200,000. The ripple voltage measured with a cathode ray oscillograph at full emission current (10 mA) of the X-ray tube was 0.03 V peak to peak.

The variable additional voltage v was obtained from a rectifying circuit using the tube 1928 as current stabiliser. The voltage v was measured with a Cambridge dynamometer voltmeter which could be read better than 0.05 V on the 50-V range, which was used for $v < 40$ V. The voltmeter was calibrated against a standard cell.

Adjustments

The bending of the crystal was controlled optically by means of a luminous slit and a suitable microscope. The radius was found to be 1000 ± 2 mm. After adjusting the crystal opening, the detector slit and the target to the same height, the adjustment of the slit parallel to the X-ray line was carried out by a new rapid and precise method.

Profile curves of the X-ray line were recorded using the uppermost mm and lowest mm of the slit respectively, the slit being very narrow (0.02 mm). If the slit was not exactly parallel to the X-ray line the two curves did not coincide. Differences in the position of the lines of about 0.005 mm could be measured. By means of a lever arrangement the slit was turned to the right position. When these adjustments were carried out the slit was broadened and a profile curve using the whole length of the slit (8 mm) was recorded (see "Measurement of the wavelength"). By taking four curves at different distances of the slit with respect to the crystal, the position of best focusing could be determined.

Measurement of the wavelength

The intensity as a function of the micrometer reading for CaO $K\alpha_1$ and $K\alpha_2$ is shown in Fig. 5. The left curve recorded with a slit width of 0.080 mm, the right one with 0.146 mm. Since only one of the edges of the slit was movable there is a corresponding displacement of the curves. Observe that the projection of the slit on the tangent to the Rowland circle is 2 times the width of the slit. (The glancing angle was 30°.)

Each curve is the sum of two curves, one recorded from left to right and the other from right to left. These curves coincided within the error of measurement.

The larger slit width, mentioned above, was used in recording the isochromats. (The smaller slit gave about the same isochromat, but with a 2-fold decrease in counting rate.) The peak value of the $K\alpha_1$ line can certainly be read off from Fig. 5 with an accuracy of 0.01 mm or 20 ppm (parts per million).

Another source of error is the focussing-defect which for the glancing-angle (30°)

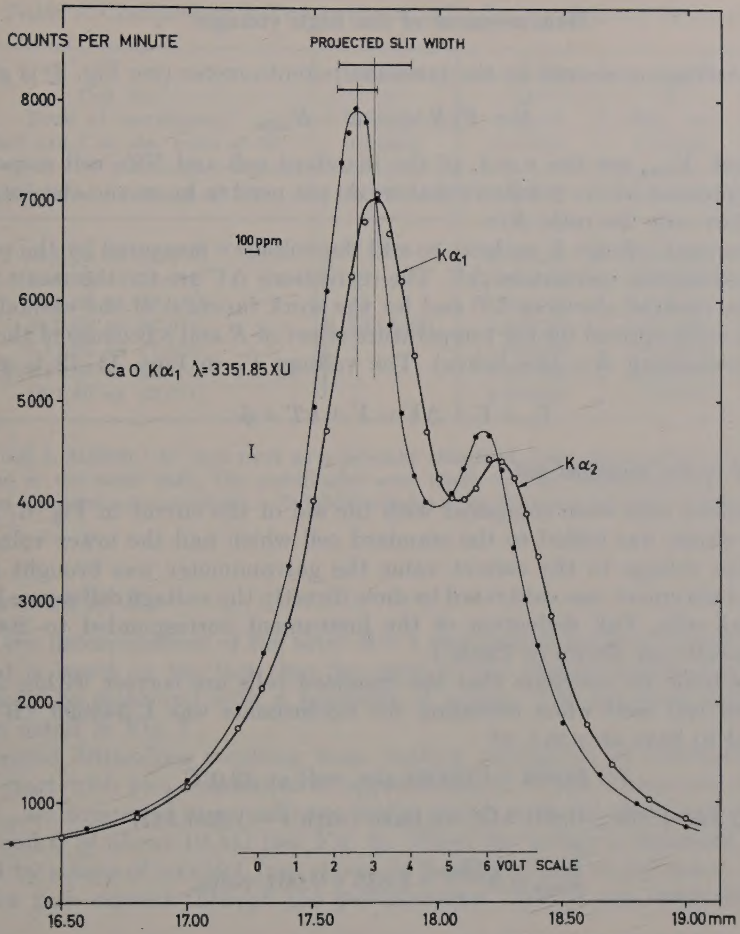

Fig. 5. The intensity distribution of the CaO $K\alpha_1\alpha_2$ lines, plotted against the reading of the micrometer screw.

and crystal opening (12 mm) in question is of the order of 0.01 mm along the Rowland circle corresponding to 20 ppm. The error in the determination of the wavelength of the $K\alpha_1$ line of CaO is certainly less then 10 ppm. Taking the mean square value of these errors we have

$$\lambda_s = 3351.85 \pm 0.10 \text{ XU} \quad (\pm 30 \text{ ppm}).$$

During the measurement of λ_s the temperature of the crystal was $23.^\circ 0 \pm 0.5$; slightly higher than the room temperature ($22.^\circ 0$) This was also the case when recording the isochromats. Thus no temperature correction was needed.

Measurement of the high voltage

The high voltage measured by the precision potentiometer (see Fig. 3) is given by

$$V = E(R/r) + E + E_{\mathrm{Nife}},$$

where E and E_{Nife} are the e.m.f. of the standard cell and Nife cell respectively. From the expression above it follows that we do not need to know the absolute values of R and r but only the ratio R/r.

To this constant voltage V we have to add the voltage v measured by the precision voltmeter and certain corrections ΔV. The corrections ΔV are for the mean thermal energy of the emitted electrons kT and for the work function of the cathode ϕ. No correction is to be applied for the temperature effect of R and r because of the special method of measuring R/r (see below). The voltage V_0 in Figs. 11–13 is given by

$$V_0 = V + \Delta V = V + kT + \phi.$$

The e.m.f. E of the standard cell

Four standard cells were compared with the aid of the circuit in Fig. 6. A small additional voltage was added to the standard cell which had the lower voltage. By adjusting this voltage to the correct value the galvanometer was brought to zero. The current instrument was calibrated to show directly the voltage difference between the standard cells. Full deflection of the instrument corresponded to 200×10^{-6} volts. The results are shown in Table 1.

From this table we conclude that the standard cells are correct within 20 ppm. The standard cell used when recording the isochromats was L-345999 "B" which was assumed to have an e.m.f. of

$$1.01854 \pm 0.00002 \text{ abs. volt at } 22.0°\text{C}.$$

Since r_{Nife} was $4.710 \pm 0.001\ k\Omega$, we have (with $r = 1.250\ k\Omega$)

$$E_{\mathrm{Nife}} = E\frac{r_{\mathrm{Nife}}}{r} = 3.838 \pm 0.001 \text{ volts.}$$

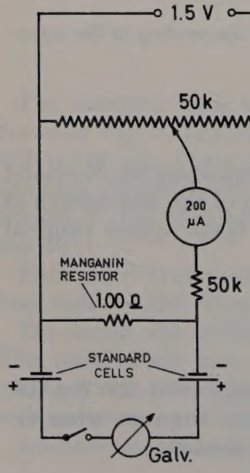

Fig. 6. Circuit used when comparing the standard cells.

Table 1. Comparison between the standard cells (Weston Normal cells).

Cell No.	L-345999 "A"	L-345999 "B"	L-346016 "A"	L-346016 "B"
Date of certificate	28.4.58	28.4.58	May '59	May '59
Certified e.m.f. in abs. volts at 20°C	1.01862	1.01861	1.01860	1.01858
Calculated e.m.f. at 22°C	1.01854	1.01853	1.01852	1.01850
18.9.59 at 22.0°C	1.018540	1.018541	1.018495	1.018494
19.9.59 at 22.0°C		1.018541	1.018496	1.018495
23.9.59 at 22.0°C		1.018541	1.018498	1.018496
25.9.59 at 22.0°C		1.018540	1.018495	1.018493
2.11.59 at 21.8°C		1.018540	1.018495	1.018492
14.11.59 at 22.1°C		1.018542	1.018495	1.018492
16.1.60 at 22.2°C		1.018541	1.018494	1.018492

The cell L-345999 "A" was used as a primary standard. Cells designated "A" and "B" were mounted in the same case. The certificates were made out by Cambridge Instrument Co. Ltd. Certified temperature correction: -0.00004 volt for a rise of temperature of 1°C between 15°C and 25°C.

Measurement of R/r

For the determination of the ratio R/r a new precise method was developed. This method is based on the fact that the ratio of two approximately equal resistances can easily be measured with a precision of 1 ppm. The precision potentiometer is seen in detail in Fig. 7.

To avoid difficulties resulting from contact resistances or thermoelectric forces, let us start with two resistances of approximately 10 kΩ. These two resistances R_0 and R_{10} are compared in an ordinary bridge circuit with the aid of two other resistances P and Q of about 10 kΩ (see Fig. 8). When the bridge is balanced, P and Q are shifted by means of a switch (not shown in the figure) and we get a new value $Q + \Delta Q$ of Q for zero current through the galvanometer. Now it can easily be shown that

$$R_{10} = R_0\,[1 + \tfrac{1}{2}(\Delta Q/Q)].$$

Thus to know R_{10} in terms of R_0 to an accuracy of 1 ppm we need only know $\Delta Q/Q$ to, say, 10,000 ppm if $\Delta Q < 0.0001\,Q$.

In the present experiment ΔQ_{10} was $-0.10 \pm 0.02\ \Omega$ corresponding to $R_{10} = 9999.95 \pm 0.01\ \Omega$, where we have assigned the value $10{,}000.00\ \Omega$ to R_0.

Combining R_0 and R_{10} in series gives a resistance R'_{20} of

$$19999.95 \pm 0.01\ \Omega\ (\pm 0.5\ \text{ppm}).$$

R'_{20} is then compared in the same way as above with a new resistance R_{20} of approximately 20 kΩ. R_{20} is then known in terms of R_0 to an accuracy of about 1.5 ppm.

Accurate values of R_{40} (≈ 40 kΩ), R_{80} (≈ 80 kΩ) and R_{160} (≈ 160 kΩ) can be obtained in the same way.

R_0, R_{80}, and R_{160} in series give a resistance R'_{250} of about 250 kΩ. Together with R_{250} (≈ 250 kΩ) we eventually get R'_{500} (≈ 500 kΩ).

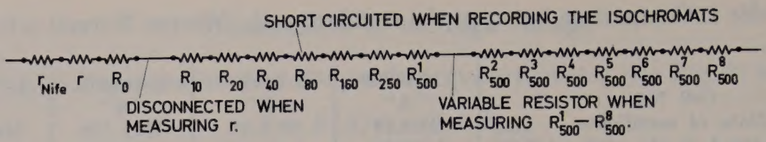
SHORT CIRCUITED WHEN RECORDING THE ISOCHROMATS
r_Nife r R_0 R_10 R_20 R_40 R_80 R_160 R_250 R¹_500 R²_500 R³_500 R⁴_500 R⁵_500 R⁶_500 R⁷_500 R⁸_500
DISCONNECTED WHEN MEASURING r.
VARIABLE RESISTOR WHEN MEASURING R¹_500 – R⁸_500.

Fig. 7. The resistors used in the precision potentiometer in Fig. 3 seen in detail.

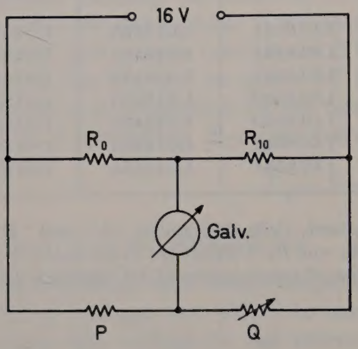

Fig. 8. Bridge circuit.

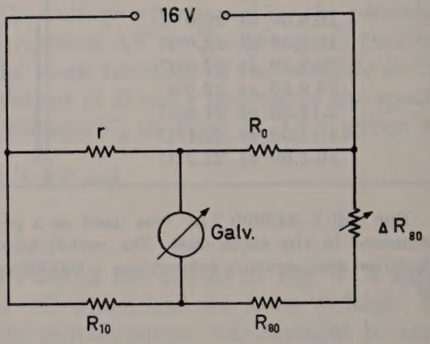

Fig. 9. Circuit used for measurement of r.

By adding small resistance (manganin wires) all the resistances R_{10}, R_{20}, R_{40}, R_{80}, R_{160} and R_{250} were made to differ by only a few ppm from the corresponding resistances R'_{10}, R'_{20} . . . R'_{250}. The remaining eight 500 kΩ-resistances were measured by connecting a variable resistance to either R'_{500} or R_{500}, depending on which of them was larger.

The resistance $r(=1.25\,\text{k}\Omega)$ was measured by means of R_0, R_{10} and R_{80}. The resistances were connected as in Fig. 9. A small resistance ΔR_{80}, which could be varied in order to balance the bridge, was in series with R_{80}. Thus we have

$$r = R_0[R_{10}/(R_{80}+\Delta R_{80})].$$

The resitance r could be measured to an accuracy of 5 ppm, since R_{10} was known to 1 ppm and R_{80} to 2.5 ppm.

Now r was determined at 16 V and 32 V over the bridge and no significant difference could be observed. On reversing the current, differences of not more than 2 ppm appeared, due to thermoelectric forces which, however, were eliminated by simply taking the average value. In measuring resistances of 10 kΩ and higher, no such effect was observed.

Great care was taken to eliminate contact resistances. Thus all critical connections were made of 1 mm copper plate and fastened by screws. For interchanging the resistances P and Q, a switch of excellent quality made by Otto Wolf in Berlin was used.

The deflection of the galvanometer was very stable during all measurements (1 mm deflection corresponded to 1 ppm or less except for r and R_{80} when it corresponded to 2 ppm). In all measurements (except for r) the voltage over the bridge was adjusted to give the same current (0.8 mA) through the resistors $R_0, R_{10} \dots R_{500}$. Thus for R_{10} the voltage was 16 V and for R_{500} 800 V. For that reason P and Q were 10 kΩ when

Table 2. Measurements of the precision resistances relative to R_0.

Resistor	Resistance value in terms of R_0 at 22.0°C ohms		Error in ppm	Power dissipation in watts	
				Rated	Actual
r	1,250.000	−0.063	5	0.5	0.0008
R_0	10,000.00	reference	—	0.5	0.006
R_{10}	10,000.00	−0.05	1	0.5	0.006
R_{20}	20,000.00	−0.13	1.5	0.5	0.013
R_{40}	40,000.00	−0.30	2	0.5	0.025
R_{80}	80,000.00	+0.6	2.5	0.5	0.05
R_{160}	160,000.0	+0.5	3	1.3	0.10
R_{250}	250,000.0	+0.7	4	2	0.16
R_{500}^{1}	500,000.0	−62	5	4	0.32
R_{500}^{2}	500,000	−146	5	4	0.32
R_{500}^{3}	500,000	−139	5	4	0.32
R_{500}^{4}	500,000	−140	5	4	0.32
R_{500}^{5}	500,000	−139	5	4	0.32
R_{500}^{6}	500,000	+58	5	4	0.32
R_{500}^{7}	500,000	+148	5	4	0.32
R_{500}^{8}	500,000	+318	5	4	0.32

R_{10}, R_{20}, and R_{40} were measured, but 500 kΩ when R_{80}, R_{160}, R_{250} and R_{500} were measured.

In Table 2 all resistances used for the measurement of R/r together with errors in ppm and mean values in terms of R_0 ($R_0 = 10{,}000.00\ \Omega$) are shown. Rated and actual power dissipation for each resistance are also included in the table. In fact the value of R/r calculated from measurements at six different occasions in two months did not vary by more than 10 ppm. This excellent reproducibility was attained by using manganin resistances of very high quality and keeping the temperature constant ($22.0° \pm 0.1$). One measurement was made with twofold current (1.6 mA) which resulted in a change in the R/r value of only about 8 ppm.

The high voltage could be chosen in steps of about 8 volts by suitable combination of the resistances $R_0, R_{10}, \ldots R_{500}$. In all recordings reported here the following resistances were used:

$$R = R_0 + R_{10} + R_{20} + R_{40} + R_{160} + R_{250} + 8 \times R_{500}.$$

The total resistance becomes (from Table 2)

$$R = 4489.901\ k\Omega\ (\pm 5\ \text{ppm}).$$

The value of r measured as described above was

$$r = 1.249937\ k\Omega\ (\pm 5\ \text{ppm}).$$

Thus we have

$$R/r = 3592.10 \quad (\pm 10\ \text{ppm}).$$

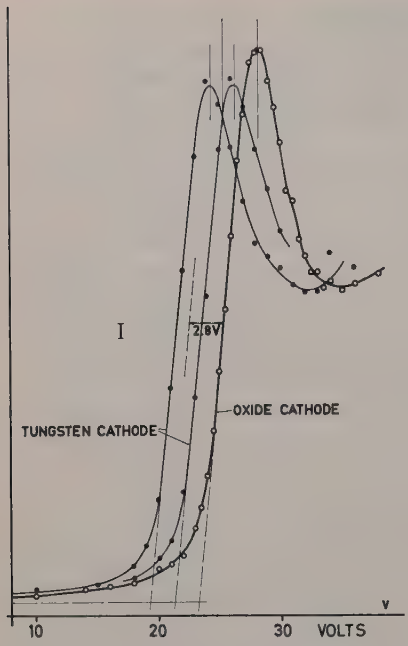

Fig. 10. Isochromats for determination of the work function of the cathode.

The method described above for measuring the ratio of two resistances has several advantages: (1) The resistances can be measured at the same current conditions as in the actual experiment. (2) The accuracy is large (~ 10 ppm). (3) The resistances can be measured without being disconnected. (4) Resistances of various orders of magnitude are available for choosing a suitable voltage.

Work function correction

The reason for making a correction of the voltage for the work function of the cathode has been discussed previously in a number of papers [1–4, 6]. The problem is no longer *if* we should apply such a correction, but to determine the exact *magnitude* of the correction. For pure W the work function is rather well-defined (≈ 4.52 eV), but for oxide-cathodes the work function may have any value between ~ 1 and 2.5 eV, depending on the composition and formation of the oxide-layer. Therefore a determination of the work function of the oxide cathode used was made relative to a tungsten cathode.

The tungsten cathode consisted of a hair-pin shaped tungsten wire (length 16 mm and diameter 0.2 mm), which was heated by a DC current of about 4.5 A. The voltage across the wire was 2.03 V.

Isochromats were recorded with both oxide cathode and tungsten cathode. The results are shown in Fig. 10. The voltage displacement (= 2.0 V) of the tungsten isochromats results from a change in the sign of the cathode potential. Because of the greater energy spread of the emitted electrons for the tungsten cathode, the first peak is not as sharp as for the oxide cathode, and consequently no exact determination of the position of the peak was possible. However if the curves are normed as shown in the figure it is seen that the first very straight part (~ 2.5 V wide) of the isochromat is practically unaffected by an increase of the voltage spread. This is to be expected if the spread is not too large (in this case it must be less than 2 V; probably 1–1.5 V). Therefore, as a measure of the displacement between the tungsten and oxide curves, the distance between two points in the middle of the straight part was chosen, as shown in the figure. The displacement becomes 2.8 V. We must, however, subtract 0.2 V because the temperature of the standard cell was 1.5° lower when recording with the tungsten cathode. The room temperature was 22.0°, but the temperature of the standard cell did not change more than 0.1° during the recording because of the thermic insulation of the cell. The temperature coefficient of the cell was -0.0004 per degree.

The work function of the oxide cathode was calculated as follows:

$$\phi = (4.5 + 0.2) - (2.6 + 0.1) = 2.0 \text{ eV},$$

where the quantities 0.2 and 0.1 are the mean thermal energy of the emitted electrons for tungsten and oxide cathode respectively. The value 2.0 eV seems to be reasonable in view of the fact that oxide cathodes in ordinary radio tubes are not intended to be exposed to air. Similar determinations on other "home-made" cathodes at an early stage of this investigation resulted in work function values of the order of 1.5 eV.

The error in the ϕ-value given here was due to difficulties in finding corresponding points in the isochromats and to reproducibility errors. These errors, together with errors in the mean thermal energy of the emitted electrons, were estimated to 0.3 volts. Thus we have

$$\Delta V = \phi + kT = 2.1 \pm 0.3 \text{ volts}.$$

Calculation of V_0

From the preceding sections we have

$$E = 1.01854 \text{ volts} \quad (\pm 20 \text{ ppm});$$

$$R/r = 3592.10 \quad (\pm 10 \text{ ppm});$$

$$E_{\text{Nife}} = 3.838 \text{ volts} \quad (\pm 0 \text{ ppm});$$

$$\Delta V = 2.1 \text{ volts} \quad (\pm 81 \text{ ppm}).$$

Thus

$$V = 3663.56 \pm 0.08 \text{ abs. volts} \quad (\pm 22 \text{ ppm})$$

and

$$V_0 = 3665.7 \pm 0.3 \text{ abs. volts} \quad (\pm 84 \text{ ppm}).$$

Results

Three different metals were investigated: W, Mo and Ta. Every curve is the mean of two similar recordings, where the voltage was increased in one case and decreased in the other, the total counting time per point being 6 minutes.

The results of the measurements are shown in Figs. 11, 12 and 13. The target temperature was about 1200° (measured by an optical pyrometer) in each case to avoid contamination of the target. This temperature was, however, not critical. Thus for W, which is a very suitable metal because of its high intensity and high melting point, investigations at different temperatures between 900° and 1600° showed no significant changes in the isochromats.

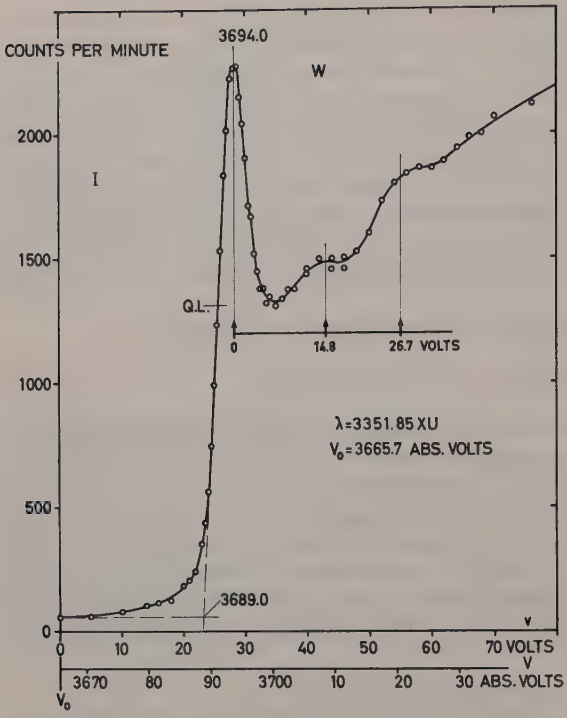

Fig. 11. Isochromat for tungsten at the wavelength of CaO $K\alpha_1$.

On the other hand, when the target was *effectively cooled* the isochromat in Fig. 11 did not appear at all. Instead an isochromat of very low intensity (about a 10-fold decrease in counting rate), which was displaced about 5 volts to higher voltages appeared. This isochromat was not as reproducible as the others. Moreover the target, when held at temperatures of the order of 1000°, was absolutely clean, while the cool target was discoloured. Bearden *et al.* [3, 4], however, working with better vacuum conditions, were able to use cool targets and got isochromats very similar to those in Figs. 11, 12 and 13. Moreover, very recently P. Johansson, using a cool target, found a W-isochromat at ~ 5 kV of almost exactly the same shape as the one in Fig. 11. For details see [17].

For the reasons mentioned above, therefore, we reject the isochromats obtained with cool targets. The similarity between these isochromats and those recorded by Nilsson and Ohlin [7] in 1946 suggests that a contamination effect could be present in their curves too. Another reason to reject these cool target curves is that they do not fit into the voltage dependence of the structure (see Fig. 15).

Discussion and interpretation of the isochromats

The interpretation of the isochromats given here is essentially the same as the one discussed by Albert [8] and later by Ulmer and Vernickel [5] (originally by Nijboer [9]). The structure near the short-wavelength limit can be regarded as a superposition of two structures, one structure due to electrons with an energy corresponding to the

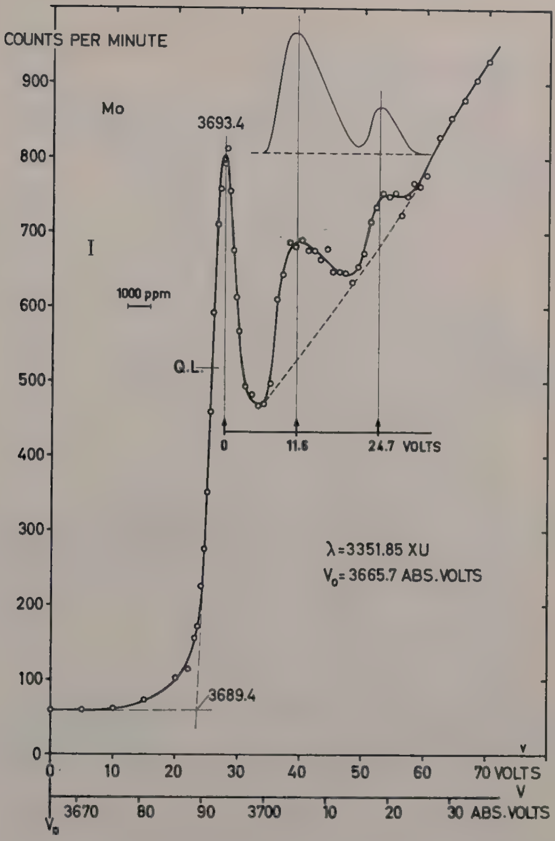

Fig. 12. Isochromat for molybdenum at the wavelength of CaO $K\alpha_1$.

whole accelerating voltage V, and one structure due to electrons having lost more or less energy by collision processes in the target. The structure of the first type should be a picture of the density of the unfilled levels near the Fermi level. Suppose the level density is as shown in Fig. 14*a*.

As is well known [10], energy losses of electrons in solids can occur only in certain amounts, so-called characteristic energy losses. These characteristic energy losses $e\,\Delta V$ are of the order of tens of a volt. Therefore, besides the primary electrons, only electrons of energy $e(V-\Delta V)$ will be present in the solid. This is true for energies 30–40 eV below the primary energy. For lower energies the energy losses overlap. The structure due to electrons of energy $e(V-\Delta V)$ should have the same shape as the one in Fig. 14*a*, but displaced to higher voltages by the amount ΔV (see Fig. 14*b*). In Fig. 14*c* is shown as an example the case where we have two energy losses $e\,\Delta V_1$ and $e\,\Delta V_2$. The resulting isochromat is simply the sum of Fig. 14*a* and *b*.

The discussion above is, of course, highly schematic. In the first place, the level density curve is smoothed out because of the limited resolving power of the apparatus used. Moreover, characteristic energy loss spectra actually are not discrete, but consist of rather broad lines [10].

Unfortunately, reliable values of characteristic energy losses are not yet available.

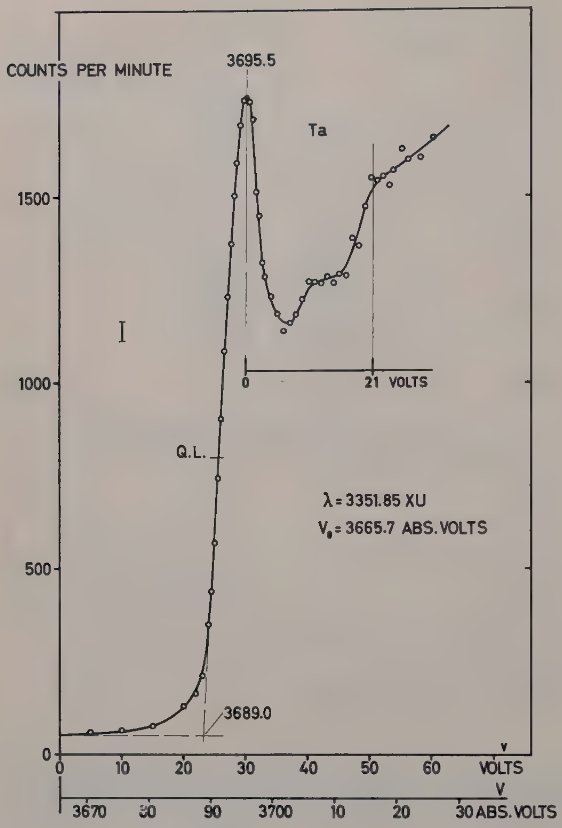

Fig. 13. Isochromat for tantalum at the wavelength of CaO $K\alpha_1$.

As a matter of fact, values found by different investigators may differ considerable. However, for W the dispersion of the values is small, a recent determination being made by Harrower [11]. He also investigated Mo at the same time and with the same apparatus.

Isochromats for W and Mo

Now let us look at the isochromats of W and Mo in Figs. 11 and 12. The peaks (except the first one) are very small and this fact makes it difficult to determine the position of the peaks better than within 1–2 volt. Therefore the position of the characteristic energy loss peaks according to Harrower [11], measured from the first peak in the isochromats, are marked. We see that the agreement is very good indeed. This agreement might of course be accidental. However, there is a number of facts which militate against such an explanation.

Albert [8] found stepwise increases or breaks for W, in the region 20–100 volts behind the quantum limit. The voltage interval between the breaks was about 25 V, which is almost exactly the second characteristic energy loss for W. The periodical breaks can be explained as a 1-fold, 2-fold, 3-fold ... energy loss. Because of the low

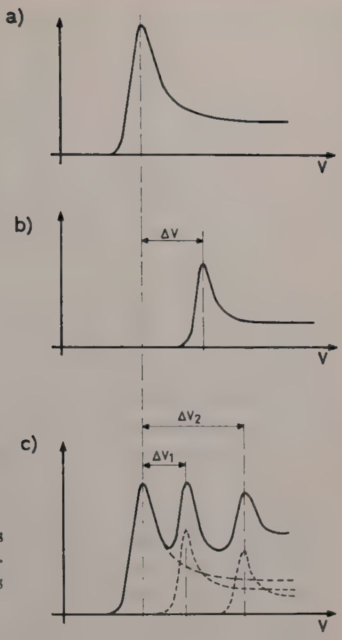

Fig. 14. Structure due to (*a*) the primary electrons; (*b*) electrons having suffered a characteristic energy loss $e\Delta V$; (*c*) the combined effect of (*a*) and (*b*) for the case of two energy losses $e\Delta V_1$ and $e\Delta V_2$.

intensity he could not observe the peaks mentioned above but looked for breaks, which is another way to attack the same problem.

Voltage dependence of the structure

The voltage dependence of the structure lends further support to the interpretation of the isochromats given here. In Fig. 15 isochromats found for different voltages (1.25 kV, 3.7 kV, 10 kV and 19 kV) are plotted. The curves are normalised to the same height for the first minimum and displaced a little with respect to each other in the y-direction. The curve for 3.7 kV (not the same as in Fig. 11) is found in the present investigation. Though the curves are not recorded with the same monochromator half-width, it is obvious that there is a general tendency for the *first peak* to decrease as the voltage increases. This fact, which also is the case for Ta and Mo, has interesting consequences.

Suppose the structure from 0 to, say, 30 volts were represented by one phenomenon only, for example, the density of the unfilled levels near the Fermi level. Then the intensities of the peaks would not change relative to each other when the voltage was changed, because the level density is an intrinsic property of the metal in question. Now the second and third peaks remain unchanged (see Fig. 15) with respect to the voltage and therefore we conclude that they do not have the same origin as the first peak.

Comparison with X-ray absorption spectra

From X-ray absorption spectra we can receive information about the level density above the Fermi level. However, because of selection rules, K, L_{I}, L_{II}, L_{III}, M_{I} ...

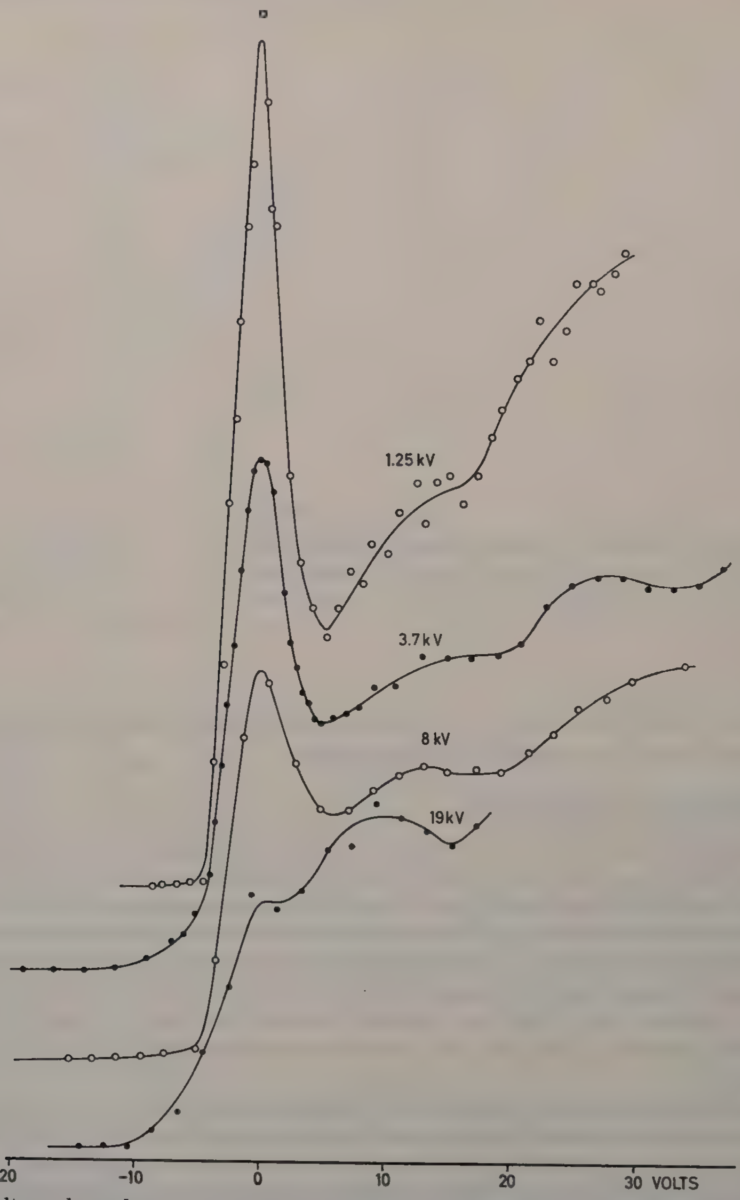

Fig. 15. Voltage dependence of the structure. The 1.25-kV isochromat was reported by Ulmer and Vernickel [5], the 8-kV and 19-kV isochromats by Bearden and Schwartz [3], and the one at 3.7 kV was found in the present investigation.

absorption edges reflect different parts (band of *s*, *p*, *d*, ... character) of the total density of the unfilled levels. Therefore it is hard to determine the appearance of the total level density from X-ray absorption spectra because we do not know how to add the different *s*, *p*, *d* ... bands. For W, for example, theoretical work by M. F.

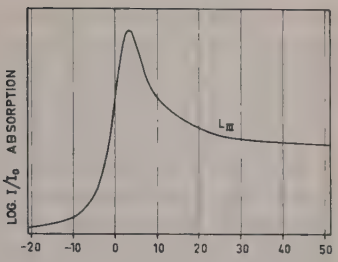

Fig. 16. L_{III} absorption edge for W reported by Bearden and Snyder. [13].

Manning and M. I. Chodorow [12] has shown that the $5d$ band will dominate strongly. Thus L_{II} and L_{III} absorption spectra alone should give a rather accurate picture of the total level density. Fig. 16 shows an L_{III} absorption edge for W reported by Bearden and Snyder [13]. From this figure it can be seen that the shape of the curve is very similar to the one assumed in Fig. 14*a*. Also, the theoretical curve fits the experimental one very well.

Thus the structure in the isochromat for W can be explained by assuming that the electrons hitting the target occupy levels of different symmetry (s, p, d, ... character) with equal probability. The assumption that the electrons prefer d states of course also explains the structure but this limitation is not needed for W.

Theoretical work on Mo is unfortunately not available, but the experiments [14] show two very narrow peaks (so-called "white lines" in X-ray spectroscopy) just above the absorption edge in the L_{II} and L_{III} spectra. The K and L_I absorption edges have no "white lines" for Mo or W. Now, the Mo-atom has five $4d$-electrons; a situation similar to that for the W atom which has four $5d$-electrons (the d shell is about half-filled). For both these metals we should expect a dominating d band in the solid state. Thus the structure of Mo can be explained in the same way as for W.

The isochromat of Ta

Consider the Ta isochromat in Fig. 13. The shape of the isochromat is very similar to that for W. This is to be expected since Ta is the element preceding W in the periodic table. It has thus only three $5d$-electrons, to four for W. The characteristic energy loss marked is the only one as yet avialable for Ta, and has been measured by Kleinn [15]. At about 11 volts there seems to be a characteristic energy loss, which has not been found by Kleinn. This is not strange, however, because Kleinn, working with 35 kV-electrons, did find the energy loss peak at 27 volts for W but not the 15-volt peak.

A most interesting property of the Ta isochromat which strongly supports the interpretation discussed in this paper is the position of the first peak. In comparison with the W isochromat a displacement of 1.5 volts to higher voltages is found. This can also be seen from Bearden's [4] isochromats. In the theoretical work [12] mentioned above it is pointed out that the level density curves found for W can also be used with good approximation for Ta if the Fermi level is displaced a certain amount to lower energies to account for the decrease in the number of electrons. Therefore, because the Fermi level has to be found at the same voltage in the isochromats, a displacement of the peak to higher voltages is to be expected.

Moreover, study of L_{II} and L_{III} absorption spectra [16] will show that the appearance of the edges for Ta and W is almost identical. Unfortunately, the edges for Ta are not distinct enough to make a direct comparison of the position of the peaks with respect to the Fermi level.

Angular dependence of the structure

With the apparatus used in the present experiment the angle θ between the electron beam and the X-rays could be varied. An experiment with $\theta = 45°$ and $30°$ was performed, keeping the angle between the electron beam and the target surface unchanged. The isochromats (for W) found were identical to those found for $\theta = 0$. However, use of a single crystal target might yield a different result.

On the other hand, the relative intensity (*not* the position) of the first peak seems to be slightly dependent on the angle φ between the electron beam and the target surface. Thus the curve in Fig. 11 was found for $\varphi \approx 84°$ and the curve in Fig. 15 for $\varphi \approx 76°$. A similar dependence was found for Mo. However, the effect might be due to other circumstances. If there is really an angular dependence, it probably has something to do with the angular dependence of the characteristic energy losses.

K. Ulmer and H. Vernickel [5] also found a difference in the height of the first peak between two W isochromats at 1.25 kV, but no angular data were reported. The difference seems to be too large to be explained as solely a temperature effect.

Isochromats of other metals

According to the interpretation given above, the shape of an isochromat is determined mainly by two different effects: (1) The total density of the unfilled levels near the Fermi level; (2) the characteristic energy losses of the primary electrons. Besides these two effects there is a smoothing effect caused by the limited resolving power of the apparatus used.

For W, the total level density function has only one sharp peak in the region 0–40 V measured from the Fermi level. Therefore the combined effect of (1) and (2) can, at least qualitatively, be resolved into its components. For other metals this can be very complicated if the level density peaks and the characteristic energy losses overlap.

Thus for Au, Cu and Pt, available K, L_{I} as well as L_{II} and L_{III} absorption spectra show no sharp peaks at all and should give isochromats without pronounced peaks. This is in fact the case, as found by different investigators [3, 8]. These isochromats, though qualitatively consistent with the interpretation given above, are hard to resolve into components.

Most interesting is an investigation of Cr and Cr_2O_3 performed recently at this Institute by P. Johansson [17].

On the determination of $V\lambda_s$

The problem of finding the quantum limit of the continuous X-ray spectrum is, if the interpretation discussed above is correct, analogous to the problem in X-ray spectroscopy to find the Fermi level in X-ray absorption spectra. The usual method in X-ray spectroscopy is to choose the inflexion point of the steep rise of the absorption edge.

In Figs. 11–13 the point Q.L. (Quantum Limit) corresponds to the least square adjusted value of $V\lambda_s$ 12372.44 kV × XU. We see that it lies very near to the inflexion point for Mo and W, but not for Ta. (For Cu the discrepancy would be even larger.)

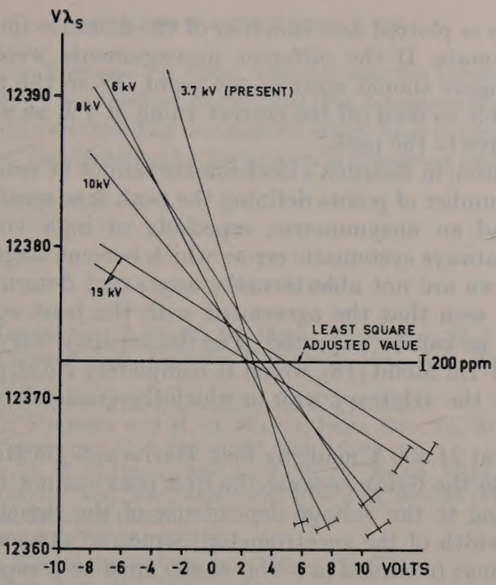

Fig. 17. The value of $V\lambda_s$ as a function of the difference $V_{\text{peak}} - V$. Observe the accumulation of intersecting points around the least square adjusted value 12372.44 kV × XU. The average value is 12372.4 for $V_{\text{peak}} - V = 3.0$ V, which is in good agreement with 2.8 ± 0.5 V found in the present work.

This is not so strange because the exact structure very close to the Fermi level is smoothed out owing to the limited resolving power of the apparatus. In fact, if the level density varies very strongly near the Fermi level, which seems to be the case for W, Mo and Ta, the Fermi level might be situated anywhere within ≈ 1 volt and still give the same shape of the isochromats. Therefore it seems impossible to make any *exact* determinations of $V\lambda_s$ from the high-frequency limit of the continuous X-ray spectrum.

However, from the interpretation given here, it follows that for the same metal the position (in volts) of the first peak *measured from the Fermi level* should be independent of the voltage of the X-ray tube. The first peak (pronounced only for a few metals) can thus be regarded as a sort of fixed point against which we can make measurements. By recording isochromats at two different voltages the uncertainty in the position of the Fermi level can then be eleiminated. The voltage–wavelength conversion factor in this case is given by

$$\frac{V_2 - V_1}{\lambda_1 - \lambda_2}\,\lambda_1\lambda_2,$$

where λ_1 and λ_2 are the wavelengths used and V_1 and V_2 the voltages corresponding to the first peak. Note that systematic errors due to the work function of the cathode and the mean thermal energy of the emitted electrons are completely eliminated.

A determination of $V\lambda_s$ using the method sketched above was not possible since only one voltage was used. However a comparison can be made with other values found for the first peak by Bearden *et al.* [3, 4]. Thus in Fig. 17 the value of $V\lambda_s$

for different voltages is plotted as a function of the distance (in volts) from the first peak in the isochromats. If the different measurements were absolutely correct, all the lines in the figure should meet in one point. From the position of this point we should then be able to read off the correct value of $V\lambda_s$ as well as the position of the Fermi level relative to the peak.

Now the peak position in Bearden's isochromats cannot be read off very accurately, partly because the number of points defining the peak is so small, and partly because the peaks are broad an unsymmetric, especially at high voltages (see Fig. 15). Moreover, there are always systematic errors which become larger (in volts) at higher voltages. Therefore we are not able to make any exact determination of $V\lambda_s$ from the figure, but it is seen that the agreement with the least square adjusted value 12372.44 is as good as can be expected. The discrepancy varying with the voltage, found by Cohen and Du Mond [18], which is completely ruled out by this fact, must be an effect due to the arbitrary way in which the quantum limit point was chosen previously.

The measurement at 24,500 V made by Felt, Harris and Du Mond [1] unfortunately cannot be included in the figure because the first peak cannot be read off. This is to be expected according to the voltage dependence of the structure (see above), and owing to the large width of the spectrometer "window". The very broad peak seen in the 24 kV-isochromat (recorded in 5-volt steps) must be a superposition of the first and second peak. With this interpretation the curve fits the others rather well.

Note that no voltage dependence of the position of the peak with respect to the quantum limit can be deduced from Fig. 17.

The method demonstrated above for the determination of $V\lambda_s$ can be used for any metal having isochromat peaks sharp enough. Thus Ta and Mo measured at 3.7 kV (see Figs. 11 and 12) and 8 kV give reasonable results. However, to obtain very accurate results the measurements must be performed on the same apparatus and in the range 1–6 kV, where the first peak in the isochromat is pronounced. Such measurements on various elements at the same time would be a test of the validity of the interpretation given here.

Errors

A survey of the estimates of the maximum errors involved in the voltage and wavelength measurements is given below. The accidental error is the mean deviation (0.1 volts) of the position of the isochromats for different runs of the same metal.

	Ppm
Standard cells	20
Ratio R/r	10
Nife cell	0
Additional voltage v	14
Voltage correction ($\phi + kT$)	81
Zero point drift of the galvanometer	5
Wavelength error according to page 311	30
Mean square value	91
Accidental error	28
Sum	119

Thus the total error (maximum error) in the voltage indication (in abs. volts), given in Figs. 11, 12 and 13, becomes ± 120 ppm or ± 0.45 volts.

ACKNOWLEDGEMENTS

I am greatly indebted to Professor Per Ohlin, who initiated this investigation, for his interest in this work. Furthermore, I am indebted to Fil. kand. Per Johansson for many valuable discussions and especially for his own recording on tungsten, which lends support to this investigation. I also wish to thank Doc. Carl Nordling for his interest in discussing problems that have arisen.

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REFERENCES

1. G. L. Felt, J. N. Harris, and J. W. M. Du Mond, Phys. Rev. *92*, 1160 (1953).
2. P. Ohlin, Inaugural Dissertation, Uppsala University, 1941, Ark. Mat., Astronom. Fys. Ser. *27*A, No. 10. (1941).
3. J. A. Bearden and G. Schwartz, Phys. Rev. *79*, 674 (1950).
4. J. A. Bearden, F. T. Johnson and H. M. Watts, Phys. Rev. *81*, 70 (1951).
5. K. Ulmer and H. Vernickel, Z. f. Phys. *153*, 149 (1958).
6. W. K. H. Panofsky, A. E. S. Green and J. W. M. Du Mond, Phys. Rev. *62*, 214 (1942).
7. Å. Nilsson and P. Ohlin, Ark. Mat. Astronom. Fys. *33*A, No. 23 (1946).
8. L. Albert, Z. Physik *143*, 513 (1955).
9. B. R. A. Nijboer, Physica *12*, 461 (1946).
10. L. Marton, Adv. in Electronics and electron Phys., vol. VII.
11. G. A. Harrower, Phys. Rev. *102*, 340 (1956).
12. M. F. Manning and M. J. Chodorow, Phys. Rev. *56*, 787 (1939).
13. J. A. Bearden and T. M. Snyder, Phys. Rev. *59*, 162 (1941).
14. A. E. Sandström, Nova Acta Reg. Soc. Upsaliensis *9*, 92 (1935).
15. W. Kleinn, Optik *11*, 226 (1954).
16. D. Coster and A. Bril, Physica *10*, 391 (1943).
17. P. Johansson (to be published in Ark. f. Fys., 1960).
18. E. R. Cohen and J. W. M. Du Mond, Encyclopedia of Physics, vol. XXXV, p. 43 or Rev. Mod. Phys. *27*, 372 (1955).

Tryckt den 23 september 1960

Uppsala 1960. Almqvist & Wiksells Boktryckeri AB